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The Application of the Electronic Balance in High Precision Pycnometry

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KEYWORDS

Density measurement, electronic balance, laboratory glassware calibration, liquid density, mass, pycnometry, volume calibration.

ABSTRACT

Pycnometers are used to measure the density of fluids. Usually pycnometer volume is determined by measuring the mass and temperature of contained water and thereafter is used to determine the density of contained fluids by further weighing. The calibration and use of the pycnometer can be achieved on a modern electronic balance without the use of the usual set of mass standards. This paper explores the electronic balance application to pycnometry, presents supporting data with analysis and discusses a pycnometer design.

INTRODUCTION

Pycnometers are essentially flasks whose internal capacity has been determined by weighing the vessel empty and again when filled with water. The pycnometer can then be filled with a liquid of unknown density and, from a similar set of weighings, the unknown density of the liquid is determined. Pycnometers are usually constructed from glass and designed to minimize the filling errors associated with setting the liquid level and trapped gas. Unlike the stable mass of a laboratory weight, the contained water mass is likely to vary significantly from filling to filling. In addition, the density of water is about 1 g/cm^3 , eight times less than that of the typical stainless steel mass standard used in balance calibration, the resulting difference in volume necessitates a large buoyancy correction. Other pycnometer characteristics that make weighing the pycnometer more difficult than laboratory weights are its propensity to become electrically charged and its hygroscopic surface.

PYCNOMETER CALIBRATION

The pycnometer calibration consists of two parts, weighing the pycnometer when empty and again when filled with water. The first observation is of the force, F_{PE} , imposed upon the electronic balance by the empty pycnometer less its buoyant force, as follows:

$$F_{PE} = M_p \left(1 - \frac{\rho_a}{\rho_p} \right) g = KO_E \quad (1)$$

where:

- M_p = mass of pycnometer
- ρ_a = air density
- ρ_p = pycnometer body density, handbook value
- K = constant of proportionality
- O_E = balance observation, empty pycnometer
- g = local acceleration of gravity

The second force, F_{PF} is similar to the above except that the pycnometer is now full of water:

$$F_{PF} = \left[M_p \left(1 - \frac{\rho_a}{\rho_p} \right) + M_w \left(1 - \frac{\rho_a}{\rho_w} \right) \right] g = KO_F \quad (2)$$

where:

- M_w = mass of water
- ρ_w = water density
- O_F = balance observation, full pycnometer

Additional information is required to determine the water mass contained in the pycnometer. The mass of an object (in this case water) must be tied to the International System of Units (SI) by calibration of the balance using a weight of known mass and density (calibration weight). Many electronic balances perform the calibration automatically and an adjustment is made to the circuit such that $K = 1$. Therefore, the pycnometer calibration process would begin with a balance calibration immediately prior to the weighing process.

The force, F_C , imposed on the balance by the calibration weight, S , during the calibration procedure can be expressed as follows:

$$F_C = S \left(1 - \frac{\rho_a}{\rho_s} \right) g = KO_C \quad (3)$$

where:

- ρ_s = density of calibration standard
- O_C = balance reading when calibration weight is engaged

The above equations are solved for the contained mass of water, M_w . The balance is set during the calibration process such that the indication is zero with the pan empty. With knowledge of the water temperature, t , the water density can be calculated from the formula discussed later. The resultant is the pycnometer volume, V_t , given by the following equation:

$$V_t = S \frac{\left(1 - \frac{\rho_a}{\rho_s}\right) \left(\frac{O_F - O_E}{O_C}\right)}{\rho_w - \rho_a} \quad (4)$$

The above solution for the pycnometer volume assumes that the air density has remained constant during the weighings and the balance calibration.

Furthermore, the air and the pycnometer and its contents are assumed to be in thermal equilibrium with each other. For this reason the pycnometer displacement volume does not manifest itself and the pycnometer density term is not present. In the above equation it also has been assumed that the balance has been zeroed before the empty and full weighings and the capacity of the flask is at the temperature of the water. The nominal value of the built-in calibration weight, S , is usually adjusted by the balance manufacturer to be accurate within the least significant digit displayed by the balance and may not need additional calibration for this application. Furthermore, it has been assumed that the weight is made from a material with a density near 8.0 g/cm^3 . If necessary the weight can be calibrated in situ or removed from the balance for determining both its mass and density⁽¹⁾.

In practice the pycnometer is filled in a constant temperature bath and the bath temperature, i.e. the temperature of the pycnometer and its contents, may be different from the temperature in the balance case at the time of weighing. The above weighing equations require modification in order to account for variations in temperature.

The empty weighing can again be expressed as a force equation as is the associated balance calibration:

$$F_{PE} = M_p \left(1 - \left(\frac{\rho_{aE}}{\rho_p}\right)X\right)g = K_E O_E$$

and the balance calibration:

$$F_{CE} = S \left(1 - \frac{\rho_{aE}}{\rho_s Z_1}\right)g = K_E O_C$$

where:

- ρ_{aE} = air density during empty weighing
- Z_1 = $1/[1 + 3 \alpha (t_{aE} - t_{ref})]$, thermal expansion of S
- α = linear thermal expansion coefficient of S
- X = $1 + 3 \beta (t_{aE} - t_{ref})$, thermal expansion of pycnometer
- ρ_p = handbook density of pycnometer body at t_{ref}
- β = linear thermal expansion coefficient of pycnometer, handbook value

t_{ref} = reference temperature for object of interest
 t_{aE} = air temperature
 ρ_{aE} = air density

Two similar force equations can be written for the weighing of the pycnometer when filled with water:

$$F_{PF} = \left[M_p \left(1 - \left(\frac{\rho_{aF}}{\rho_p} \right) Y \right) + M_w \left(1 - \frac{\rho_{aF}}{\rho_{wf}} \right) \right] g = K_F O_F$$

$$F_{CF} = S \left(1 - \frac{\rho_{aF}}{\rho_S Z_2} \right) g = K_F O_C$$

where:

ρ_{wf} = water density
 ρ_{aF} = air density during full weighing
 ρ_S = density of calibration weight at t_{ref}
 Z_2 = $1/[1 + 3 \alpha (t_{aF} - t_{ref})]$, thermal expansion of S
 Y = $1 + 3 \beta (t_w - t_{ref})$, thermal expansion of pycnometer
 t_w = water temperature during the weighing
 ρ_w = water density at t_w
 t_{aF} = air temperature
 ρ_{aF} = air density

We assume with proper attention to thermal soaking that the water temperature is the same as the air temperature.

The volume of the contained water is the mass of the water divided by the density of the water. We note that the density of the water is calculated using the temperature of the bath at the time of the filling. The pycnometer capacity, V_{bt} , at the bath temperature is:

$$V_{bt} = \left[S \frac{\left(1 - \frac{\rho_{aF}}{\rho_S Z_2} \right)}{\left(\frac{O_C}{O_F} \right)} - Q \frac{\left(1 - \frac{\rho_{aE}}{\rho_S Z_1} \right)}{\left(\frac{O_C}{O_E} \right)} \right] / \left[\left(1 - \frac{\rho_{aF}}{\rho_{wf}} \right) \rho_{wbt} \right] \quad (9)$$

$$Q = \frac{1 - \left(\frac{\rho_{aF}}{\rho_p} \right) Y}{1 - \left(\frac{\rho_{aE}}{\rho_p} \right) X}$$

The balance observations are assumed to have been corrected for any nonlinear balance response if required. A detailed discussion of the balance linearity test and corrections is given in the companion paper by Schoonover and Jones ⁽¹⁾.

The term Q requires an approximation (handbook value) for the density of the pycnometer body.

The pycnometer volume is standardized to a reference temperature of 25 °C. The following relationship is used:

$$V_{25} = V_{bt} (1 + 3\beta(25^\circ\text{C} - bt))$$

where:

V_{25} = volume of pycnometer at 25 °C

V_{bt} = volume of pycnometer at bt , bath temperature

APPARATUS

The Electronic Balance

A short summary of the principles of operation is given here. A more thorough overview of these instruments is given in ^(1,2,3,4). Detailed knowledge of the electronic circuits is unnecessary. Fig. 1 illustrates the basic principles of an electronic balance, and a representative mechanical structure is shown in Fig. 2. When a downward force is applied to the balance pan (loaded with an object) it is opposed by a magnetic force generated by the interaction of two magnetic fields. One field is generated by a permanent magnet and the other a controllable electromagnet. Usually, the magnetic force is applied through a multiplying lever and not by direct levitation. Sufficient magnetic force is generated to restore the mechanism (pan) to its unloaded position (null point) relative to the balance structure. It is desirable in common weighing applications to tie the magnetic force to the unit of mass via calibration of the electronic circuit. The circuit is adjusted such that the algebraic sum of the gravitational and buoyant forces produces a balance indication approximately equal to the nominal value of the applied mass. In mass calibration work the applied mass, i.e. calibration weight, usually has a density of about 8 g/cm³.

In this application a balance with a capacity of at least 150 g was required. A balance with a capacity of 200 g was selected. The manufacturer's specifications were a standard uncertainty of 0.0001 g with a maximum nonlinearity of 0.0002 g. The level of repeatability was found to be better than the manufacturer's claim.

Pycnometer

The pycnometer is fabricated from borosilicate glass with a linear coefficient of thermal expansion of 0.0000033 °C⁻¹. The configuration of the pycnometer is shown in Fig. 3. Each of the capillaries have an internal diameter of approximately 0.65 mm. The wire plugs shown do not fit perfectly (see discussion). The exterior surface of the pycnometer was coated with a nearly invisible layer of tin oxide to prevent the build-up of static charge.

Constant Temperature Water Bath

The constant temperature water bath was set to a temperature very close to 25 °C, the reference temperature for the pycnometer. The variation of the temperature in the bath was controlled to ± 0.003 °C per hour. The pycnometer was contained in a brass sleeve that was sealed at the bottom and suspended in such a manner that the sleeve and the pycnometer were completely surrounded (inside and out) by the bath water. The sleeve and the pycnometer were raised to the water surface for insertion of the plugs and drying the interior of the bowl. In this way the bowl of the device was briefly exposed for setting the water level.

Water Bath Thermometer

A two-probe thermistor thermometer with a standard uncertainty of 0.003 °C was used to measure the water temperature in the bath. The thermometer probes were inserted into the space between the wall of the brass sleeve and the pycnometer body. An average of the two readings was used in the calculations.

Air Density and Water Density

Air Density

There are three parameter measurements required to calculate the air density: air temperature, barometric temperature and relative humidity. The air temperature measurements were made in the balance case using a mercury thermometer with an uncertainty of 0.05 °C. Barometric pressure was measured with an aneroid barometer with a standard uncertainty of 13.3 Pa (0.1 mmHg) and relative humidity was measured with a capacitance-type humidity probe with a standard uncertainty of 5% relative humidity. The latter two instruments were located in the laboratory, close to the balance. A value of 0.043% was used for the content of atmospheric carbon dioxide present.

The air density equation used in this work is the CIPM 1981/91 recommendation⁽⁵⁾. This formula ties its predecessor, CIPM-81, to the International Temperature Scale of 1990 (ITS-90) and utilizes better estimates for the values of some of the constants and other parameters.

Uncertainties in the values of the temperature, pressure and relative humidity do affect the uncertainty of the calculated air density. Our standard uncertainty estimate for the density of air is presented Table 1. The companion paper presents an alternate air density equation that is easier to implement⁽¹⁾.

Water Density

The work of Kell⁽⁶⁾ is generally regarded as the comprehensive treatment of water density. The Kell formula provides a value for the density of air-free water at 101.3250 kPa (1 atmosphere) of pressure with an estimated standard uncertainty of about 1.7 ppm. The formula assumes the use of the IPTS-1968 (t68) temperature scale and temperatures measured in terms of the IPTS-1990 (t90) must be converted to IPTS-1968. This is readily accomplished in the range between 20 °C and 30 °C from the following approximate relationship⁽⁷⁾:

$$t_{90} - t_{68} = - 0.006 \text{ }^{\circ}\text{C}$$

The water temperature measurements here are estimated to have a standard uncertainty of 0.003 °C, with a negligible effect on the water density.

ANALYSIS

This method described by Ku⁽⁸⁾ (which is consistent with NIST policy⁽⁹⁾) has been used to propagate standard uncertainties in the functional relationship, $f(X_1, X_2, \dots, X_n)$, of the uncorrelated variables X_1, X_2, \dots, X_n . Table 1 presents for each variable its value, the estimated standard uncertainty, u_i , and an evaluation of the partial derivatives. At the bottom of the table is the estimated combined standard uncertainty for the function as given by the following relationship, where V_t is the volume of the pycnometer:

$$(u_{c_{V_t}}) = \left[\sum_{i=1}^n \left(\frac{\partial f}{\partial Y_i} \right)^2 (u_i)^2 \right]^{\frac{1}{2}} \quad (12)$$

The effect of each variable in Table 1 is calculated from the product of the standard uncertainty and the partial derivative for that particular variable. For convenience to the reader we list the partial derivatives below. We have chosen to propagate the standard uncertainties through the simple form of equation (4) rather than the more complex form of equation (9). The resulting uncertainty analysis from the following equations is nearly the same and is easier to perform. The reader can use these derivatives to evaluate their own standard uncertainty using the applicable standard uncertainties of their equipment.

$$\frac{\partial V}{\partial S} = \frac{\left(1 - \frac{\rho_a}{\rho_s} \right) \left(\frac{O_F - O_E}{O_C} \right)}{\rho_W - \rho_a}$$

$$\frac{\partial V}{\partial \rho_s} = \frac{S \left(\frac{O_F - O_E}{O_C} \right) \left(\frac{\rho_a}{\rho_s^2} \right)}{\rho_W - \rho_a}$$

$$\frac{\partial V}{\partial \rho_a} = S \frac{\left(\frac{O_F - O_E}{O_C} \right)}{(\rho_W - \rho_a)^2} \left(1 - \frac{\rho_W}{\rho_s} \right)$$

$$\frac{\partial V}{\partial \rho_W} = \frac{-S \left(1 - \frac{\rho_a}{\rho_S} \right) \left(\frac{O_F - O_E}{O_C} \right)}{(\rho_W - \rho_a)^2}$$

$$\frac{\partial V}{\partial O_E} = \frac{-S \left(1 - \frac{\rho_A}{\rho_S} \right)}{O_C (\rho_W - \rho_A)}$$

$$\frac{\partial V}{\partial O_F} = \frac{-S \left(1 - \frac{\rho_a}{\rho_S} \right)}{O_C (\rho_W - \rho_a)}$$

$$\frac{\partial V}{\partial O_C} = \frac{-S \left(1 - \frac{\rho_a}{\rho_S} \right) (O_F - O_E)}{O_C^2 (\rho_W - \rho_a)}$$

One important parameter in the uncertainty analysis is the balance reproducibility, as measured by the standard uncertainty. The balance used here, like many electronic balances, performs better when lightly loaded, as in the case of the pycnometer weighings. Its standard uncertainty was found to be 42 μg from 0 to 130 g and 118 μg at 200 g. These standard uncertainties are combined in quadrature with the standard uncertainty of the linearity correction⁽¹⁾. With hindsight (see discussion) the application of a linearity correction to the balance observations was not justified with respect to the reproducibility of the pycnometer volume achieved here.

As previously noted, the balance weighings were repeated 6 times during each weighing cycle and is reflected in Table 1. It is noteworthy that the balance calibration reproducibility (42 μg) is not improved by repeated calibration cycles and therefore is only performed once. This standard uncertainty cannot be obtained explicitly but, from the nature of digital circuits, it is known to be less than 1/2 count, i.e. 50 μg . The standard uncertainty component would then be $[(1/2)/\sqrt{3}]$ because all values between -1/2 count and +1/2 count are equally probable. The value used here (42 μg) was determined by repeated weighings at the 100-g level. The pycnometer calibration results did not justify this much rigor.

The root-sum-square, RSS, given in Table 1 provides a satisfactory standard uncertainty estimate for the volume of the pycnometer. However, we note again and discuss later that the pycnometer volume is not constant but varies with filling errors that can only be determined experimentally. Based upon the

analysis given in Table 1 we would expect to determine the pycnometer volume with a standard uncertainty of about two parts per million, ppm.

TABLE 1. Standard Uncertainty Budget for the Pycnometer Calibration.

Parameter	Value	u_i	Partial	Effect
S (std. mass)	100 g	0.00005 g	$0.700736 \text{ cm}^3/\text{g}$	0.000035 cm^3
ρ_s (std. den.)	8.0 g	0.00032 g/cm^3	$0.000013 (\text{cm}^3)^2/\text{g}$	negligible $<< 10\text{E-}8 \text{ cm}^3$
ρ_a (air den.)	0.0012 g/cm^3	0.0000003 g/cm^3	$61.397265 (\text{cm}^3)^2/\text{g}$	0.000018 cm^3
ρ_w (H ₂ O den.)	1.0 g/cm^3	0.0000017 g/cm^3	$-70.157778 (\text{cm}^3)^2/\text{g}$	0.000119 cm^3
O_E (bal. obs.)	64 g	$0.000042/\sqrt{6} \text{ g}$	$-1.001051 \text{ cm}^3/\text{g}$	0.000017 cm^3
O_F (bal. obs.)	134 g	$0.000042/\sqrt{6} \text{ g}$	$1.001051 \text{ cm}^3/\text{g}$	0.000017 cm^3
O_C (intrinsic)	100 g	0.000049 g	$-0.700736 \text{ cm}^3/\text{g}$	0.000034 cm^3
			$u_c = \text{RSS} =$	0.000132 cm^3 (1.9 ppm)

DATA

The pycnometer underwent five independent volume determinations. That is, after each set of empty and full weighings the pycnometer was emptied, cleaned and refilled. Each filling was accomplished by siphoning hot distilled water through the pycnometer body by way of the capillaries until the water overflowed into the overflow bowl to a level such that it would cover the ends of the capillaries. The bowl was then capped and the pycnometer and its contents were soaked in a constant temperature water bath until thermal equilibrium was achieved. Then, the water temperature was recorded and the overflow bowl was partially emptied. The plugs were then promptly inserted into the capillary openings and the rest of the excess moisture was wicked away with small pieces of filter paper.

The overflow bowl was then covered and the exterior of the pycnometer was carefully dried. The pycnometer was then stored in the balance for 24 hours to achieve thermal and hygroscopic equilibrium with the air in the balance case, before the weighing commenced. For the empty weighings the pycnometer was inverted and emptied until no visible water was present. The interior was dried by passing dry nitrogen gas through the capillaries. Of course, the same

attention must be paid to the thermal soaking of the empty pycnometer in the balance.

This procedure was repeated five time and the results reported in Table 2. The combined standard uncertainty, u_c , was found to be 40 ppm with 4 degrees of freedom, d.f. Note that if the first measurement were to be omitted the standard uncertainty would be lowered to 24 ppm. Although there is insufficient data to justify discarding the data point we feel that we were still learning in that portion of the exercise and that repeated measurements would validate this assertion.

Based upon an analysis of Table 1 we projected a standard uncertainty of about 1.9 ppm but observed an experimental standard uncertainty of 40 ppm. The model did not account for filling errors. Possible improvements to reduce these standard uncertainties are discussed later.

TABLE 2. Calibration Results of the High Precision Pycnometer.

Run	Capacity @ 25 °C
1	70.86937 cm ³
2	70.87351 cm ³
3	70.87429 cm ³
4	70.87736 cm ³
5	70.87438 cm ³
Mean	70.87378 cm ³
u_c (4 d.f.)	0.00286 cm ³ 40 ppm

DISCUSSION

There is a 38 part per million (ppm) difference between the standard uncertainty projection of Table 1 and the experimental standard uncertainty found in Table 2. We believe the major source of the discrepancy results from filling errors. It is believed that with further experience that an experimental standard uncertainty of 20 ppm could easily be obtained without any changes in the present procedure. This would lower the difference of the projected versus experimental standard uncertainty to about 18 ppm. To obtain further improvement, the filling errors must be reduced. The plugs used in this experiment did not provide a fixed pycnometer volume. This condition could be improved by replacing the straight plugs with tapered glass plugs made from the same borosilicate glass. We believe that this improvement, along with tapered seats in the ends of the capillaries would yield an experimental standard uncertainty of 10 ppm or better.

When the pycnometer is made to work reliably at the 10 ppm level it would be competitive with high-accuracy hydrostatic weighing methods used to determine liquid densities with less attendant difficulties.

It is not unusual for a high precision electronic balance to have a nearly ideal

linear response. The lack of linearity, at its worst, is usually not more than 2 ppm of full scale and somewhat better on the higher quality balances. Therefore, it is unnecessary to apply linearity corrections without significant improvement in the pycnometer performance.

The need of many users would be well-served by accepting the mass and density values reported by the balance manufacturer for the built-in calibration weight. Users requiring higher accuracy can determine the mass and density of the built-in weight themselves or by an appropriate laboratory.

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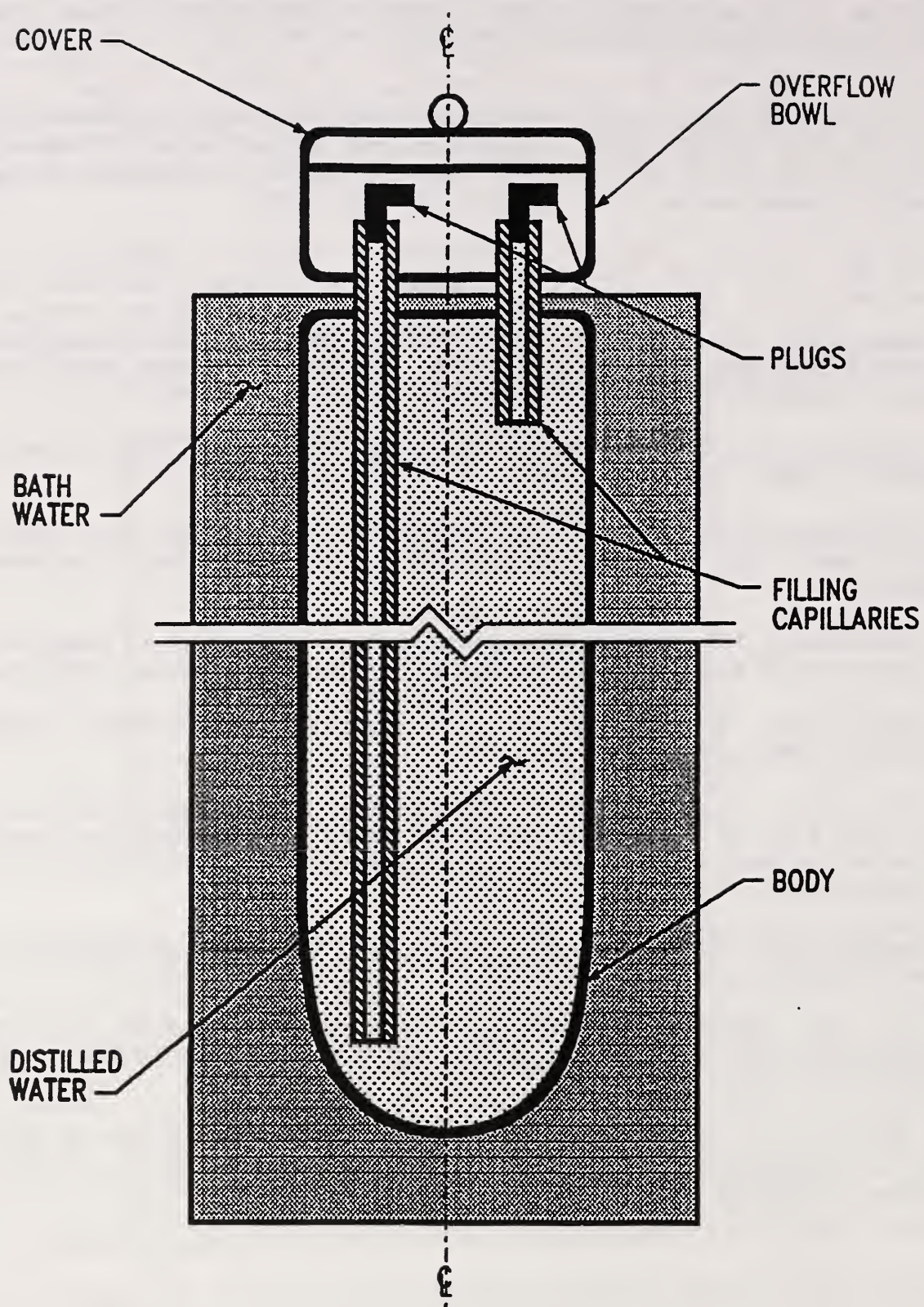


Figure 3. High Precision Pycnometer

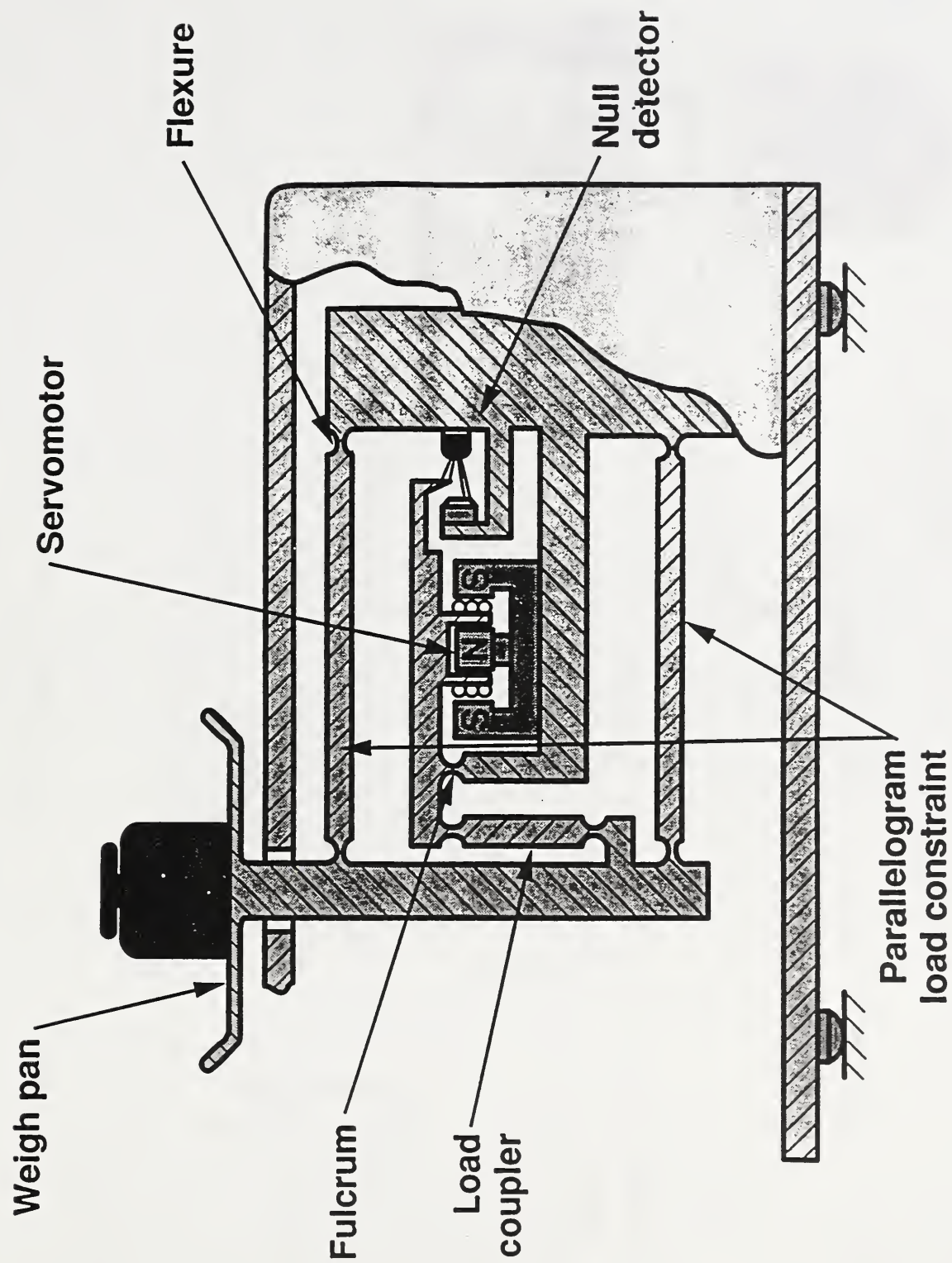


Figure 2. Typical Mechanical Structure of the Electronic Balance

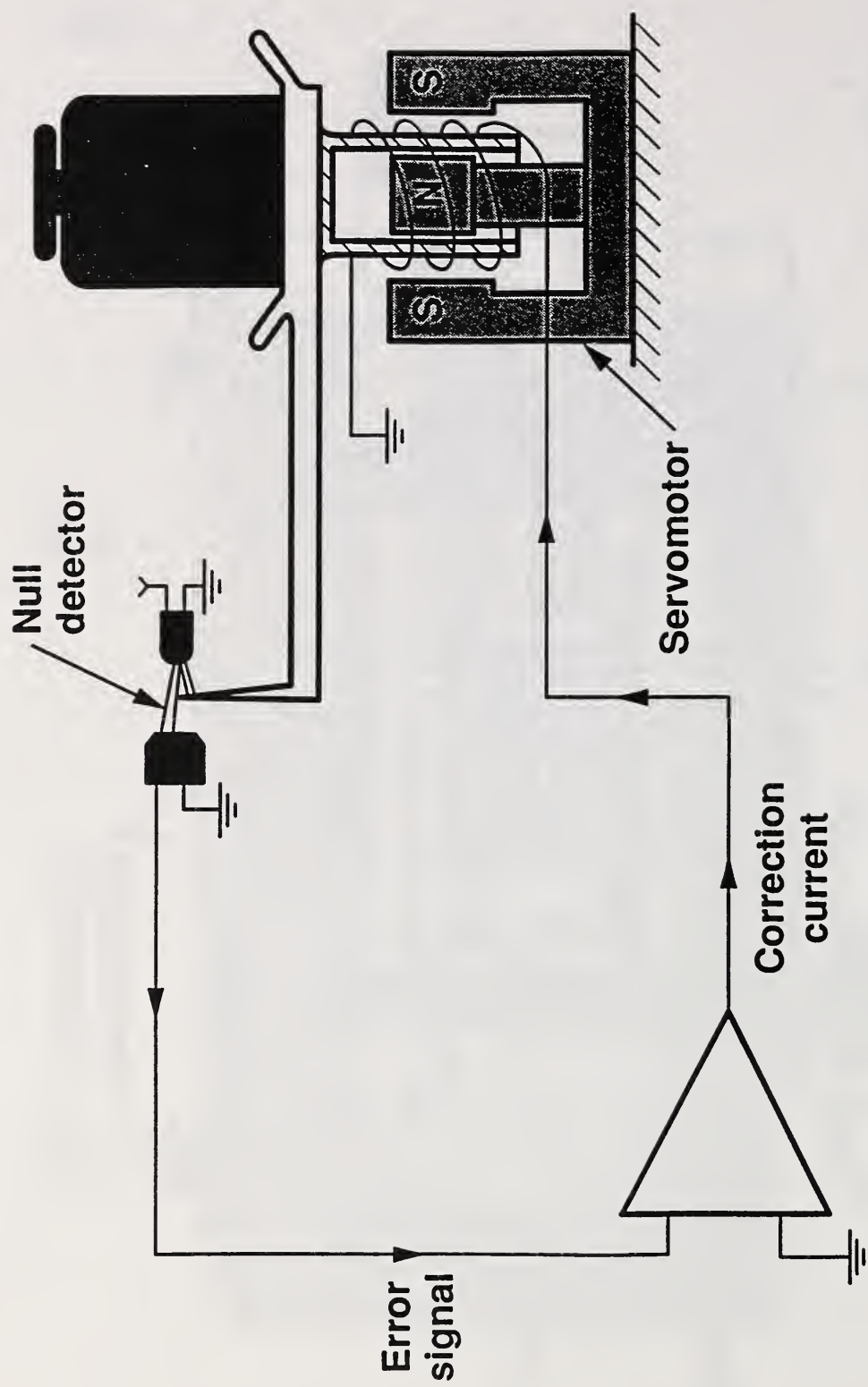


Figure 1. Basic Principles of the Electronic Balance

